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SECURITY CLASSIFICATION OF THIS PAGE

AD-A212 360 REPORT DOCUMENTATION PAGE

1a. REPORT SECURITY CLASSIFICATION: Unclassified	1b. RESTRICTIVE MARKINGS
2a. SECURITY CLASSIFICATION AUTHORITY	3. DISTRIBUTION/AVAILABILITY OF REPORT: Approved for public release; distribution unlimited.
2b. DECLASSIFICATION/DOWNGRADING SCHEDULE	
4. PERFORMING ORGANIZATION REPORT NUMBER(S): 4	5. MONITORING ORGANIZATION REPORT NUMBER(S): ARO 22388.8-MS
6a. NAME OF PERFORMING ORGANIZATION: North Carolina State University; 6b. OFFICE SYMBOL (If applicable)	7a. NAME OF MONITORING ORGANIZATION: U. S. Army Research Office
6c. ADDRESS (City, State, and ZIP Code): Raleigh, NC 27695-	7b. ADDRESS (City, State, and ZIP Code): P. O. Box 12211, Research Triangle Park, NC 27709-2211
8a. NAME OF FUNDING/SPONSORING ORGANIZATION: U. S. Army Research Office; 8b. OFFICE SYMBOL (If applicable)	9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER: DAAG29-85-K-0128
8c. ADDRESS (City, State, and ZIP Code): P. O. Box 12211, Research Triangle Park, NC 27709-2211	10. SOURCE OF FUNDING NUMBERS: PROGRAM ELEMENT NO. / PROJECT NO. / TASK NO. / WORK UNIT ACCESSION NO.

11. TITLE (Include Security Classification): Chemical Treatment of Epoxy Resins to I. Reduce Moisture Sensitivity and II. Improve the Mechanical Properties. Unclassified.

12. PERSONAL AUTHOR(S): Richard D. Gilbert and Raymond E. Fornes

13a. TYPE OF REPORT	13b. TIME COVERED	14. DATE OF REPORT (Year, Month, Day)	15. PAGE COUNT
Final	FROM 05/01/85 TO 07/31/89	09/15/89	---

16. SUPPLEMENTARY NOTATION: The view, opinions and/or findings contained in this report are those of the author(s) and should not be construed as an official Department of the Army position, policy, or decision, unless so designated by other documentation.

17. COSATI CODES		
FIELD	GROUP	SUB-GROUP

18. SUBJECT TERMS (Continue on reverse if necessary and identify by block number): Reduced Moisture Absorption - Epoxy Resins (Unclassified)

19. ABSTRACT (Continue on reverse if necessary and identify by block number)

Epoxy resin/graphite fiber composites absorb moisture which has a deleterious effect on on composite mechanical properties. The moisture absorption results from the electrostatic attraction between residual functional groups on the epoxy resin molecules and water, blocking the functional groups with various reactants decreases the epoxy resin equilibrium moisture absorption as much as 75%. Marked isocyanates incorporated into the resin prior to curing permits in situ blocking of the functional groups, reduces moisture absorption up to 65% without affecting the elastic modulus. The resin Tg is lowered, but the stress-strain properties are generally unaffected.

20. DISTRIBUTION/AVAILABILITY OF ABSTRACT	21. ABSTRACT SECURITY CLASSIFICATION
☐ UNCLASSIFIED/UNLIMITED ☐ SAME AS RPT. ☐ DTIC USERS	Unclassified
22a. NAME OF RESPONSIBLE INDIVIDUAL	22b. TELEPHONE (Include Area Code) / 22c. OFFICE SYMBOL

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Chemical Treatment of Epoxy Resins to I. Reduce Moisture Absorption and II. Improve the Mechanical Properties

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September 15, 1989

Contract/Grant Number DAAG29 - 85 - K - 0128

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Statement of Problem

Epoxy resin/graphite fiber composites absorb significant amounts (~ 4%) of water which causes a decrease in the epoxy resin Tg, plasticization, micro-cracking, delamination, and resin-fiber debonding, resulting in a serious property loss.

The epoxy resin at its optimum degree of cure contains numerous functional groups (hydroxyl, amine, epoxide, sulfone) and the electrostatic attraction between these groups and water provide the driving force for water absorption. The amount of water uptake is determined by the unoccupied volume of the epoxy which is a function of the degree of cure. It was proposed to study the effect of blocking the functional groups, by chemical reaction with suitable reactants, on the moisture absorption. Reduction of the moisture absorption would improve mechanical properties. It was also proposed to study the use of carboxylic terminated elastomers to obtain a better property balance at higher degrees of cure.

Summary of Important Results

1. Employing thin films of the epoxy resin, it was shown by infrared spectroscopy and differential scanning calorimetry, that silylation, carbanilation, and/or cyanoethylation of residual hydroxyl, amine, and epoxy groups occurs.

2. Reductions in equilibrium moisture absorptions up to 75 percent were obtained.

3. Moisture uptake by the epoxy resin exhibits Fickian behavior at 30, 45, 55, and 70°C. The diffusion coefficient, D, increased from 30° to 55°C but decreased at 70°C, attributed to a reaction of water with residual oxirane groups.

4. Sorption of isocyanates essentially follows Fickian behavior.

5. Moisture diffusion of the films after blocking the residual functional groups by cyanoethylation or carbanilation exhibits Fickian behavior. At 30°C, D values are significantly higher for reacted films. At 70°C, the value of D is unchanged for cyanoethylated films, but D values are significantly lower for films reacted with isocyante blocking agents compared with the epoxy resin.

6. Blocking the residual functional groups of the epoxy resin with fluorinated aromatic reagents reduced the equilibrium moisture absorption by as much as 75%. Pentafluorobenzoyl chloride is a more efficient blocking reagent than fluorinated isocyanates. 2,4-Difluoro-phenyl isocyanate is a more effective blocking reagent than the trifluoromethylphenyl isocyanates due to its higher reactivity.

7. Several masked isocyanates were synthesized with variations in both the isocyanate type and masking group and were characterized by elemental analysis and NMR spectroscopy and determination of their unblocking temperatures. Those with unblocking temperatures in the 120–130°C range were incorporated into the epoxy resin prior to curing to provide *in situ* blocking of residual function groups in the epoxy resin. Infrared spectroscopy and differential scanning calorimetry demonstrated the residual functional groups were reacted. Reduction in equilibrium moisture absorptions as high as 65% were obtained, depending on the masked isocyante.

8. Dynamic mechanical analysis studies showed the Tg of the epoxy resin is lowered by incorporation of the masked isocyanate, but the elastic modulus is relatively unchanged at temperatures below Tg.

9. Stress-strain studies of the epoxy resins after curing in the presence of the masked isocyanates are relatively unaffected by incorporation of the masked isocyanate, demonstrating this approach is a practical technique for lowering the equilibrium moisture absorption of epoxy resins.

10. High resolution ^{13}C-CP/MAS NMR was used to follow the reactions of the residual functional groups with the masked isocyanates and to identify intermediates and by-products.

Publications

"Reduction in the Moisture Absorption of Cured MY 720/DDS Epoxy Resin," by C. M. Fisher, R. D. Gilbert, R. E. Fornes, and J. D. Memory, *J. Polym. Sci., Polym. Chem. Ed.*, 1985, 23, 2931.

"Chemical Modification of Cured MY 720/DDS Epoxy Resins Using Fluorinated Aromatic Compounds to Reduce Moisture Sensitivity," by H.-P. Hu, R. D. Gilbert, and R. E. Fornes, *J. Polym. Sci., Polym. Chem. Ed.*, 1987, 25, 1235.

"Sorption and Transport Properties of MY 720/DDS Epoxy Reacted with Blocking Reagents," by B. K. Kelly, R. D. Gilbert, R. E. Fornes, and V. T. Stannett, *J. Polym. Sci., Polym. Phys.*, 1988, 26, 126.

"The Effect of Masked Isocyanates on the Moisture Absorption of MY 720/DDS Epoxy Resin, by S. V. Lonikar, N. Rungsimuntakul, R. D. Gilbert, and R. E. Fornes, *J. Polym. Sci., Polym. Chem. Ed.*, Accepted for Publication.

"Solid State CP MAS ^{13}C NMR Studies of the Reaction of an Epoxy Resin with Masked Isocyanates," by S. S. Sankar, S. V. Lonikar, R. D. Gilbert, R. E. Fornes, and E. O. Stejskal, *J. Polym. Sci., Polym. Phys.*, Accepted for Publication.

"Sorption and Transport Properties of MY 720/DDS Epoxy Reacted with Blocking Reagents," *Proceedings of the Fifth International Joint Military/Government-Industry Symposium on Structural Adhesive Bonding*, pp. 471-479 (Nov. 3-5, 1987). B. K. Kelly, R. D. Gilbert, R. E. Fornes, S. Lonikar, and N. Rungsimuntakul.

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